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# CHEMISTRY OF DEFECTS AND NONEQUILIBRIUM IN THE PRODUCTION OF PORELESS FINELY CRYSTALLINE OXIDE CERAMICS

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Methods for production of poreless finely crystalline oxide ceramics are considered in the context of the chemistry of defects and nonequilibrium. The paper demonstrates the necessity of reducing the degree of nonequilibrium of the sintering process by decreasing the mass transfer by introduction of additives that produce oxygen vacancies and by reducing the probability of the appearance of local compaction.

In order to ensure high mechanical strength, ceramics ought to be poreless and consist of crystals that are as small as possible and similar in size. The problem is that in order to eliminate pores completely, one must ensure sufficiently intense diffusional mass transfer, which, however, should not be accompanied by rapid growth of the crystals.

The purpose of the study is to consider methods for production of poreless finely crystalline oxide ceramics in the context of the chemistry of defects and nonequilibrium.

For the diffusion process to be efficient, the cation and anion mass flows have to be coordinated in such a way that the total electric current is equal to zero. In the case of the vacancy mechanism of diffusion, mass transfer is determined by the vacancy flow in the cation and anion sublattices [1]

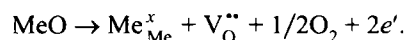
$$J_i = C_i M_i F_i,$$

where  $J_i$  is the flow of vacancies in sublattice  $i$ ;  $C_i$  is the concentration of vacancies in sublattice  $i$ ;  $M_i$  is the mobility of the vacancies;  $F_i$  is the motive force of diffusion.

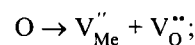
For the mass transfer to be efficient, the ratio between the cation vacancies and the anion (oxygen) vacancies should be close to the stoichiometric ratio between the cations and anions in the oxide crystal corrected for their mobility and motive force. Otherwise the mass transfer will be limited by the concentration of vacancies whose flow is below the level required to provide a total electric current equal to zero. This will disturb the electric balance and impede the diffusional mass transfer due to the appearance of an electric field oriented in such a way as to hinder the diffusional flow.

Vacancies are distinguished as thermal vacancies, whose concentration depends only on the temperature, and impurity vacancies, which depend on the concentration of impurities and additives [1]. At technological temperatures, the process is usually controlled by vacancies arising due to the presence of impurities or modifying additives.

Since the oxygen anion has higher volatility than the metal cation, in most oxides the concentration of oxygen vacancies increases at high temperatures [2]. As a consequence, oxygen vacancies  $V_O^{\bullet\bullet}$  are formed in the oxygen sublattice, especially in the boundary layers of the crystal:



An increase in the oxygen vacancy concentration  $[V_O^{\bullet\bullet}]$  produces a decrease in the concentration of vacancies in the cation sublattice  $[V_{\text{Me}}^{\bullet\bullet}]$  according to the Schottky equation:



$$K_s = [V_{\text{Me}}^{\bullet\bullet}] [V_O^{\bullet\bullet}].$$

This process is facilitated by a decrease in the size of the crystals, and it becomes more intense in highly disperse powders. The concentration of cation and anion vacancies is perceptibly affected by impurities, additives, the composition of the gas medium, and the presence of tensile and compressive stress fields in the crystal. To accelerate the vacancy diffusion, which is the most frequent type of diffusion in oxides, it is usually necessary to use additives that increase the concentration of cation vacancies. In complex oxides it is necessary

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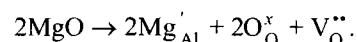
to increase primarily the concentration of the most slowly diffusing cations [2].

The diffusional mass transfer in oxides has a determining effect on many high-temperature processes in ceramics: sintering, high-temperature creep, diffusional polymorphic transitions. An increase in the concentration of oxygen vacancies will delay the diffusional mass transfer and all the enumerated processes. The smaller the particle size, the more noticeable the deviation from stoichiometry at the particle surface ought to be. The very slight growth observed in calcination of small crystals obtained chemically, for example, by the cryochemical method, can be accounted for by an increased concentration of oxygen vacancies on the surface of these crystals. The same reason accounts for the fact that samples made of highly disperse powders usually do not exhibit perceptible crystal growth before the disappearance of opened porosity. This usually happens when a relative porosity of 90% is attained and the open porosity transforms into closed porosity, both in traditional ceramics and in nanocrystalline materials [3]. It is possible that the presence of certain vacancies that impede the diffusion processes and create concentrational and electric barriers on the surface of nanoparticles can account for the possibility of producing nanocrystalline materials.

All natural processes are irreversible and nonequilibrium, and they differ only in the degree of nonequilibrium [4]. Processes evolve in stability-instability-stability series. Regions of unstable behavior of a system, namely, bifurcations, are of special significance for technology [5]. It is impossible to predict the subsequent evolution of a system in the case of bifurcation. The system acquires increased sensitivity to all external and internal effects. The purpose of a technology engineer is to organize the processes in such a way as to eliminate basic bifurcations. This can be accomplished by internal or external controlling actions on the system, which should reliably exceed the level of uncontrollable actions (noise). A substantial degree of nonequilibrium in the region of a bifurcation increases fluctuations of the system and, accordingly, the required controlling signals. Therefore, an effective and commonly used instrument consists in decreasing the degree of nonequilibrium of the process (its rate) in the region of the bifurcation [5].

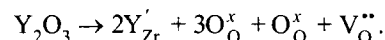
It is known that high intensity of diffusional mass transfer in sintering is expressed in rapid displacement of intercrystalline boundaries, and the growing crystals trap pores. Retardation of the crystal growth rate can prevent trapping of pores, which is used in the production of transparent ceramics. This is accomplished by decreasing the mass-transfer rate by an introducing additives that increase the concentration of oxygen vacancies. To accomplish this, the additive cation should have a lower degree of oxidation than the cation of the main material that it replaces. In such a substitution, negatively charged impurity atoms are formed, and positively charged oxygen vacancies are formed to provide electrical compensation. For example, magnesium ox-

ide additives are used to produce poreless (transparent) corundum ceramics:



Oxygen vacancies should appear as oxygen passes to the interstices and is replaced by an anion with a higher valence, such as nitrogen, but this happens much less often. It should be noted that if the diffusional mass transfer is retarded, the final-sintering temperature has to be increased. Thus, transparent corundum ceramics is sintered at a temperature around 1800°C. When using a  $\text{TiO}_2$  additive, which creates cation vacancies and intensifies the mass transfer, a dense ceramics that contains larger crystals with small intracrystalline pores is produced at a temperature around 1650°C.

Crystal growth can also be retarded by modifying the chemical composition of the crystal surface. Transparent yttrium oxide is obtained using  $\text{ZrO}_2$  as an additive. A substance enriched in  $\text{ZrO}_2$  is evidently formed on the surface of the  $\text{Y}_2\text{O}_3$  crystals.  $\text{Y}_2\text{O}_3$  is dissolved in that substance, and the resulting oxygen vacancies impede the mass transfer:



If after final removal of the pores  $\text{ZrO}_2$  completely dissolves in  $\text{Y}_2\text{O}_3$ , the resulting ceramic will be single-phase.

It is very difficult to increase the concentration of oxygen vacancies and maintain this level with increasing temperatures. An increase in the concentration of oxygen vacancies is a manifestation of negative feedback by the system, which prevents a change in its stable state. Due to the predominant volatility of oxygen, the vacancy concentration has to increase with increasing temperature. If the concentration of oxygen vacancies is too high, the system represented by a sintered ceramic sample responds to this by decreasing it. Some of the cations from the additive or the main material pass to the interstices and produce cation vacancies. Cation vacancies can also result from reactions with the ambient gas medium. This accelerates the diffusional mass transfer and contributes to a decrease in the total energy of the system.

Finely crystalline ceramics are usually produced from highly disperse powders that are prone to aggregation and local compaction [6]. A sintered sample made from highly disperse particles decreases its surface energy not by uniform shrinkage but by compaction of individual local areas. This process is facilitated by a rather high degree of process nonequilibrium. The probability of local compaction increases with increase in the powder dispersity and decrease in the sample density. Local compactations in a sample made of highly disperse powder initiate in more dense regions intense mass transfer that causes growth of crystals, and between the crystals pores are formed that are difficult to remove in the final stages of sintering.

A decrease in the degree of nonequilibrium of the sintering process decreases the probability of the appearance

of local compactions. This is facilitated by additives that cause formation of oxygen vacancies. The size of the powder particles (aggregates) should not be too small. Apparently it should not be below 1.0 – 1.5  $\mu\text{m}$ . An efficient method to decrease the degree of nonequilibrium of the sintering process is preliminary calcination of the powder, which decreases the powder activity somewhat. To reduce the probability of the local compactions, an increase in the density and equidensity of the sample is used successfully, involving appropriate methods of powder preparation and molding, such as casting and hydrostatic compression. A decrease in the degree of nonequilibrium of the process in the region of a bifurcation is facilitated by sintering carried out with a controlled rate of shrinkage [5].

Another possibility consists in increasing the degree of nonequilibrium of the process by superfast sintering [5]. As the degree of nonequilibrium increases, the size of the structural elements of the system decreases [7]. In superfast sintering of a sample, the size of its elements becomes comparable to the crystal size, and local-compaction processes do not have time to occur. The main drawback of this method is the difficulty of imparting a high amount of energy to the sample in the usual way. The sample can fail to withstand the thermal shock and may disintegrate. More promising methods involve microwave sintering and plasma-activated sintering, in which thermal energy is released in the entire volume of the sample. It is possible to increase the motive force of the sintering process and, accordingly, the degree of its nonequilibrium by applying external pressure (hot pressing). However, the pressure application procedure has to agree with the sample temperature, which determines the friction between the particles and the plastic properties of the sample. Otherwise, areas of local compaction can appear in the sample, which are joined together in a strong but hollow skeleton that can be destroyed only by application of a certain threshold pressure [7]. Use of these methods made it possible to obtain not only finely crystalline but also nanocrystalline materials [3].

It is possible to use the effect of inheriting the structure obtained in the previous stage to eliminate bifurcation [6]. The technological process should be organized in such a way as to prevent the system from creating arbitrarily sized dissipative structures for the most efficient energy dissipation and make the system use its previously developed structures for this purpose. An example is production of spherical granules by sputtering saturated solutions of the corresponding salts into the precipitator solution [8]. Another option is self-organization, which is demonstrated in aggregation of active powders in dry grinding. It is known that dry grinding of highly disperse powders increases the density of molded samples and sintered ceramics [9].

In order to obtain fine-crystalline poreless ceramics, the degree of nonequilibrium of mass-transfer processes in

sintering should be decreased and not increased. The most efficient method is the introduction of additives that decrease the diffusional mass transfer by formation of oxygen vacancies up to complete compaction of the sample. Under traditional firing conditions this would produce an increase in the sintering temperature and the energy consumption. The use of sintering with a controlled shrinkage rate and superfast sintering makes it possible to reduce the energy consumption substantially.

The most common method to form oxygen vacancies is replacement of main-material cations with cations of an additive with a lower of oxidation degree. It is quite difficult to maintain an excess in the concentration of oxygen vacancies with respect to cation vacancies at high temperatures, since cations of the additive or the main material start to pass to the interstices and produce cation vacancies.

Another possibility is superfast sintering, especially microwave or plasma sintering. Apparently, the very high degree of nonequilibrium of the process facilitates retention of a high concentration of oxygen vacancies on the crystal surface, which delays crystal growth. The probability of the appearance of local compactions can be reduced by increasing the sample density and equidensity, by decreasing the particle activity to a reasonable level by selecting their optimum size, by preliminary dry grinding of the powder, and by preliminary heat treatment of it.

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